

## **ELECTROCHEMICAL CORROSION BEHAVIOR OF CU-ZN ALLOYS IN OXY-ACID SOLUTION**

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### **ABSTRACT**

The electrochemical corrosion behavior of Cu-Zn alloys in different concentrations of H<sub>2</sub>SO<sub>4</sub> solutions was studied using potentiodynamic polarization, electrochemical impedance spectroscopy measurements. The increase in acid concentration accompanied with increases in the corrosion current density,  $I_{corr}$ , corrosion rate, C.R. also, it is observed that the anodic Tafel slope values are almost increased as the concentration of acid increased. The impedance response consisted of characteristic depressed semicircles clarifying that the corrosion process occurs under charge transfer control. The presence of 2 % Aluminum in the Alloy II improves the corrosion resistance in H<sub>2</sub>SO<sub>4</sub> media as compared to Alloy I. The charge transfer resistance values,  $R_{ct}$ , for Cu-Zn alloys (I and II) in H<sub>2</sub>SO<sub>4</sub> acid solutions follow the order: Alloy II > Alloy I. The results obtained from both methods were in good agreement.

**KEYWORDS:** Cu-Zn Alloys, Electrochemistry, Corrosion, Oxy-Acid Solution

### **INTRODUCTION**

Copper and its alloys are widely used in industry because of their excellent electrical and thermal conductivity and are often used in heating and cooling system (1). Brass has been widely used as tubing material for condensers and heat exchangers in various cooling water systems to condensate steam in turbine gas. Brass is susceptible to a corrosion process known as dezincification and this tendency increases with increasing zinc content of the brass (2). The corrosion resistance of copper alloys depends upon the formation of a protective oxide film (3). In industry, H<sub>2</sub>SO<sub>4</sub> is extensively used for acid pickling, acid cleaning and removal of rust and acid de-scaling processes (4).

The aim of the present work is to study the electrochemical corrosion behavior of two Cu-Zn alloys in different concentration of oxy-acid (H<sub>2</sub>SO<sub>4</sub>) solution

### **EXPERIMENTAL PROCEDURE**

#### **Materials**

Two types of the commercial copper alloys are used in this study having the chemical composition (wt %) are shown in Table (1). These alloys were prepared by Central Metallurgical Research and Development Institute.

#### **Surface Pretreatment of the Electrodes**

Before each experiment, the electrodes surface were mechanically polished with successive grades of 120 up to

1200 emery papers till the surface appears as a bright mirror. The electrodes were then rinsed several times with deionized water and degreased with acetone and immersed directly in the test solution.

### Electrolytic Cell

The cell (Pyrex glass) used in potentiodynamic and impedance measurements has five opening in the main joint of the vessel, three of them for the following three electrodes, the working electrode, the Pt counter electrode and the Ag/AgCl reference electrode and the other two as inlet and outlet of the gas. The cell was of double walled with two opening for the circulation of the thermo stated water.

### Electrochemical Measurements

Two different electrochemical methods were used to evaluate the corrosion behavior of Cu-Zn alloys. The potentiodynamic polarization measurements and EIS were performed using the Voltalab 40 Potentiostat PGZ301 made in Germany. The Volta Master 4 software is designed to measure and analyze corrosion rate.

#### potentiodynamic polarization

potentiodynamic polarization of the two Cu-Zn alloys were carried out at range of potential from (-800 to 1000 mV/Ag/AgCl) and scan rate 2 mV/s., then Tafel lines are plotted and the corrosion rate (C.R), corrosion potential ( $E_{corr}$ ) and corrosion current density ( $I_{corr}$ ) values were recorded.

#### Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance spectroscopy (EIS) is a powerful technique for investigating electrochemical and corrosion systems. Impedance measurements of the two Cu-Zn alloys were carried out in frequency range from (100 kHz to 100 mHz) with amplitude of 10 mV peak-to-peak using ac signals at open circuit potential. The experimental impedance was analyzed and interpreted based on the equivalent circuit. The main parameters deduced from the analysis of Nyquist diagram are the resistance of charge transfer  $R_{ct}$  and the capacitance of double layer  $C_{dl}$ . Figure 1 Show equivalent circuit model for the studied system.

## RESULTS AND DISCUSSIONS

### potentiodynamic polarization Curves

The potentiodynamic anodic and cathodic polarization curves for Cu-Zn alloys (I and II) in different concentrations of H<sub>2</sub>SO<sub>4</sub> solutions, at 25 °C are shown in figures (2 and 3). These curves reveal that, the cathodic current density which corresponds to hydrogen evolution decreases gradually reaching a definite potential value at the steady-state corrosion potential, which depends on the type of the electrode as well as on the acid concentration. On the other hand, the anodic curves in the potential range examined indicated the presence of two distinct anodic regions:

The first is characterized by a very small decrease in current density, nearly constant and independent on potential up to a certain critical potential. In the second potential region and in dilute H<sub>2</sub>SO<sub>4</sub> solutions the current,  $I$ , would change with the applied potential,  $E$ , according to tafel equation (5).

$$E = a - b \log I \quad (1)$$

### Where A and B are Constant

As indicated in Tables 2 and 3, the increase in acid concentration accompanied with increases in the corrosion current density,  $I_{corr}$ , corrosion rate, C.R. also, it is observed that the anodic Tafel slope values are almost increased as the concentration of acid increased. This behavior in two alloys may be due to increasing in hydrogen ion reduction at cathodic area and increasing sulphate ions concentration, which lead to increase in copper dissolution.

Table 2 shows that Alloy I becomes an active site with increasing the  $H_2SO_4$  acid concentrations due to the increase in corrosion rate more than Alloy II as shown in Table (3). The preferential dissolution of Zn from Cu-Zn alloys occurs more predominately with Zn rich then with Cu rich alloys (6). Little work has been reported concerning the effect of a systematic increase of zinc content or minor alloying elements such as (Al, As, Sn or Pb) on the electrochemical behavior of brass alloys (6,7,8).

The presence of 2 % Aluminum in the Alloy II improves the corrosion resistance in  $H_2SO_4$  media as compared to Alloy I. According to Roubaix(9) diagram Aluminum causes a highly beneficial hard layer of aluminum oxide ( $Al_2O_3$ ) to be found on the surface that is thin, transparent, stable and self – healing. This effect also has been attributed to the change in the microstructure, the number of defects, the segregation of the alloy and the properties or composition of the passive film formed on its surface (6). So, Aluminum in Alloy II makes brass stronger and more corrosion resistance (10).

### Electrochemical Impedance Spectroscopy Measurements

Figures (4 and 5) shows Nyquist plots for the two Cu-Zn alloys in different concentration of  $H_2SO_4$  solutions at 298 K at the respective open circuit potential. The impedance data of the Cu-Zn alloys in different concentration of  $H_2SO_4$  solutions were analyzed using the equivalent circuit shown in Figure 1. This circuit includes constant phase elements (CPE) in place of capacitors to represent various types of non-homogeneities typical of corroding electrodes such as surface roughness, insufficient polishing, grain boundaries and surface impurities (11).

The charge transfer resistance,  $R_{ct}$ , and double layer capacitance,  $C_{dl}$ , values calculated for the two Cu-Zn alloys after fitting the data are given in Table 4.

The Nyquist plots for two Cu-Zn alloys, Figures. (4 and 5), in all tested concentration of  $H_2SO_4$  solutions show a single semicircle shifted along the real impedance ( $Z_r$ ) axis and single capacitive loop, which is attributed to charge transfer of the corrosion process. The diameters of the loops decrease with the increase in the concentration of  $H_2SO_4$ . The impedance spectra consist of a Nyquist semicircle type without appearance of diffusion contribution to the total impedance  $|Z|$  indicating that the corrosion proceeds mainly under charge transfer control (12).

From the impedance data given in Table 4 of two Cu-Zn alloys in different concentration of  $H_2SO_4$  solution, the value of  $R_{ct}$  decrease and  $C_{dl}$  value increase. The decrease in  $R_{ct}$  and increase  $C_{dl}$  values with increasing in concentration of  $H_2SO_4$  suggest an increase in rate of corrosion of Cu-Zn alloys and support the observations made in the potentiodynamic polarization studies. The charge transfer resistance values,  $R_{ct}$ , for Cu-Zn alloys (I and II) in  $H_2SO_4$  acid solutions follow the order:

### Alloy II > Alloy I

This sequence reflects the beneficial effects of Al in Alloy II. The presence of 2 % Al in Alloy II improves the corrosion resistance due to formation of thin, transparent, stable and self – healing  $Al_2O_3$  layer (9).

The results obtained from the potentiodynamic polarization measurements and EIS were in good agreement.

## CONCLUSIONS

From above discussion, it is observed that:

- Corrosion current density and corrosion rate is higher in Alloy I more than Alloy II.
- The presence of 2 % Al in Alloy II improves the corrosion resistance due to formation of thin, transparent, stable and self – healing  $Al_2O_3$  layer
- The electrochemical impedance spectroscopy data observed, for charge transfer resistance ( $R_{ct}$ ), were in agreement with those obtained from the potentiodynamic polarization measurements. The charge transfer resistances value following order:

**Alloy II < Alloy I**

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## APPENDICES

Table 1: Chemical Composition (Wt. %) of the Two Copper Alloys

Alloy	Alloying Elements								
	Cu	Zn	Si	Ca	S	Al	Ni	Fe	Mn
Alloy (I) Cu-Zn	83.47	14.66	0.67	0.50	0.16	--	--	--	--
Alloy (II) Cu-Zn-Al	62.98	31.86	0.94	--	--	2.43	0.26	0.33	1.08

Table 2: Corrosion Parameters for Alloy I in Different Concentration of H<sub>2</sub>SO<sub>4</sub>, At 25 0C

Alloy (I)	E <sub>corr</sub> mV	I <sub>corr</sub> mA/cm <sup>2</sup>	$\beta_a$ mV	$\beta_c$ mV	C.R. mm/y
0.01 M	-37.7	0.0253	34.3	-160.9	0.294
0.05 M	-46.9	0.040	37.1	-268.5	0.465
0.1 M	-48.7	0.0966	41.7	-132.7	1.122
0.5 M	-52.9	0.1687	38.1	-302.8	1.960
1 M	-54.9	0.2478	39.4	-259.8	2.879

Table 3: Corrosion Parameters for Alloy II in Different Concentration of H<sub>2</sub>SO<sub>4</sub>, At 25 0C

Alloy (II)	E <sub>corr</sub> mV	I <sub>corr</sub> mA/cm <sup>2</sup>	$\beta_a$ mV	$\beta_c$ mV	C.R. mm/y
0.01 M	-305.0	0.0133	30.1	-32.7	0.154
0.05 M	-303.0	0.0254	28.2	-33.5	0.295
0.1 M	-107.0	0.0261	58.7	-124.6	0.303
0.5 M	-144.6	0.0282	50.0	-86.4	0.328
1 M	-154.7	0.0292	62.1	-102.2	0.339

Table 4: Impedance Parameters for Two Cu-Zn Alloys in Different Concentration of H<sub>2</sub>SO<sub>4</sub>, At 25 0C

Conc. of H <sub>2</sub> SO <sub>4</sub>	Alloy (I)		Alloy (II)	
	R <sub>ct</sub> ohm.cm <sup>2</sup>	Cdl $\mu$ F/cm <sup>2</sup>	R <sub>ct</sub> ohm.cm <sup>2</sup>	Cdl $\mu$ F/cm <sup>2</sup>
0.01 M	988.5	50.87	8159	27.30
0.05 M	958.5	56.29	6949	33.77
0.1 M	791.5	66.41	6278	35.48
0.5 M	690.9	164.0	3355	57.25
1 M	440.0	257.4	2096	239.8

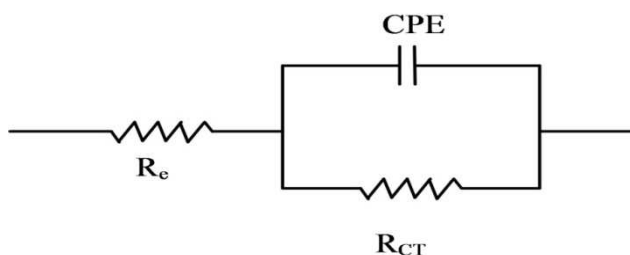
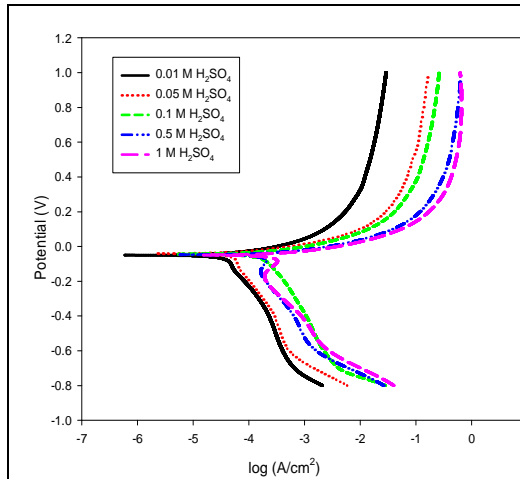
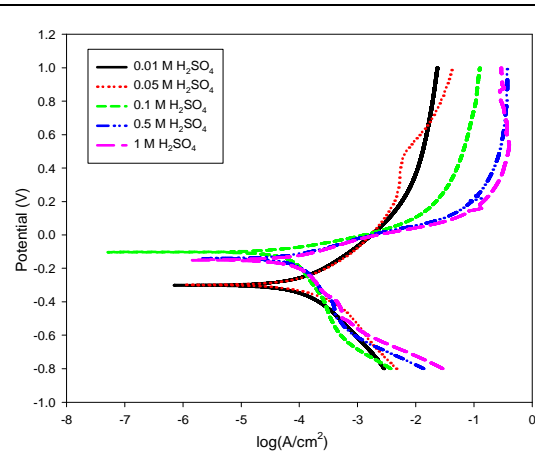


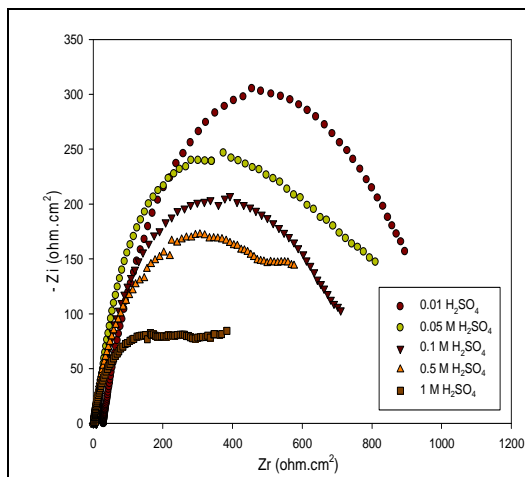
Figure 1: Suggested Equivalent Circuit Model for the Studied System



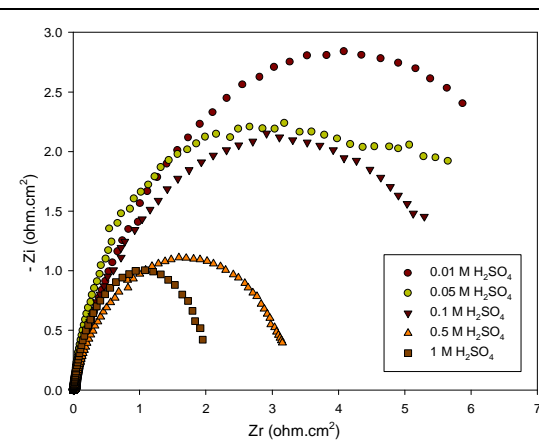
**Figure 2: Anodic and Cathodic potentiodynamic polarization Curve for Alloy I in Different Concentrations of Aerated H<sub>2</sub>SO<sub>4</sub>, at 25 0C**



**Figure 3: Anodic and Cathodic potentiodynamic polarization Curve for Alloy II in Different Concentrations of Aerated H<sub>2</sub>SO<sub>4</sub>, at 25 0C**



**Figure 4: Nyquist Plot for Alloy I in Different Concentration of H<sub>2</sub>SO<sub>4</sub>, at 25 0C**



**Figure 5: Nyquist Plot for Alloy II in Different Concentration of H<sub>2</sub>SO<sub>4</sub>, at 25 0C**